Promoting long-term cycling performance of high-voltage Li$_2$CoPO$_4$F by the stabilization of electrode/electrolyte interface

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**Fig. S1**  Crystal structure of Li$_2$CoPO$_4$F: (a) view along [100], (b) view along [010], (c) view along [001], (d) view towards (111). The CoO$_4$F$_2$ octahedra are shown in gray and the phosphate tetrahedra are shown in blue. The lithium, cobalt, phosphorus, oxygen and fluorine atoms are shown in orange, purple, blue, red and green, respectively.
Figure S2 shows $^7$Li and $^{31}$P MAS NMR spectra for Li$_2$CoPO$_4$F at different spinning frequencies.

Figure S2 shows $^7$Li and $^{31}$P MAS NMR spectra for Li$_2$CoPO$_4$F. Different spinning frequencies were applied to identify the isotropic peaks of $^7$Li and $^{31}$P for Li$_2$CoPO$_4$F. The isotropic peaks located at 1.5 ppm, -32.6 ppm and -81.8 ppm for $^7$Li, 1223.1 ppm for $^{31}$P.
Fig. S3  $^7$Li and $^{31}$P MAS NMR spectra for the Li$_3$PO$_4$, the mixture of Li$_2$CoPO$_4$F and Li$_3$PO$_4$ after ball milling and Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F samples.

In order to identify the chemical shifts of $^7$Li and $^{31}$P for Li$_3$PO$_4$, the control experiment was carried out. A mixture of pristine Li$_2$CoPO$_4$F and Li$_3$PO$_4$ was ball milled at 500 rpm for 10 h. Figure S3 shows the $^7$Li and $^{31}$P NMR spectra for the Li$_3$PO$_4$, the mixture of Li$_2$CoPO$_4$F and Li$_3$PO$_4$ after ball milling and the Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F samples. It can be seen that the chemical shifts of $^7$Li for the three samples all locate at 1.5 ppm. However, the chemical shift of $^{31}$P for the Li$_3$PO$_4$ locates at 10.0 ppm, the chemical shifts for the mixture of Li$_2$CoPO$_4$F and Li$_3$PO$_4$ after ball milling and Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F both locate at 6.0 ppm. It is speculated that the delocalized electron of carbon and Li$_2$CoPO$_4$F makes the chemical shift move upfield. Therefore, according to the control experiment, we can make a conclusion that $^7$Li (1.5 ppm) and $^{31}$P (6.0 ppm) are assigned to Li$_3$PO$_4$. 

**Fig. S4** SEM images of the (a, b) pristine and (c, d) Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F.

**Fig. S5** Cycling performances of the 0.125 Li$_3$PO$_4$-coated and 0.25 Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F samples at 2 C and 5 C. The mole ratio of Li$_2$CoPO$_4$F to Li$_3$PO$_4$ is 8:1 (marked as 0.125 Li$_3$PO$_4$-coated) and 4:1 (marked as 0.25 Li$_3$PO$_4$-coated).
Figure S2 shows the cycling performances of the 0.125 Li$_3$PO$_4$-coated and 0.25 Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F samples. It can be clearly seen that 0.25 Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F sample shows superior cycling performance than 0.125 Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F sample.

The lithium ion diffusion coefficient is evaluated according to the equation$^1$:

$$D = 0.5R^2T^2/A^2n^4F^4C^2\sigma^2$$

Where R is the gas constant, T is the absolute temperature, A is the electrode area, n is the number of electrons per molecule during reaction, F is the Faraday constant, C is the concentration of lithium ion, $\sigma$ is Warburg factor which obeys relationship with $Z_{\text{re}}$:

$$Z_{\text{re}} = R_c + R_{\text{ct}} + \sigma \omega^{-1/2}$$

Figure S6 shows the relationship between $Z_{\text{re}}$ and $\omega^{-1/2}$. The slope $\sigma$ is obtained from the linear fitting of $Z_{\text{re}}$ versus $\omega^{-1/2}$. Therefore, $D_{\text{coated}} / D_{\text{pristine}} = (\sigma_{\text{pristine}} / \sigma_{\text{coated}})^2 = 4.3$. 

**Fig. S6** The relationship between $Z_{\text{re}}$ and $\omega^{-1/2}$ at low frequencies. The inset is the Nyquist plots of the pristine and the Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F. The data were collected at the open circuit voltage. The frequency range is from 100 kHz to 0.1 Hz.
**Fig. S7** The first charge/discharge profiles of the 0.5 Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F at various rates.

The mole ratio of Li$_2$CoPO$_4$F to Li$_3$PO$_4$ is 2:1 (marked as 0.5 Li$_3$PO$_4$-coated).

Figure S7 shows the first charge/discharge profiles of the 0.5 Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F at various rates. It can be seen that 0.5 Li$_3$PO$_4$-coated sample exhibits a discharge capacity of 105 mAh g$^{-1}$ at 20 C current rate, which is only 66.0% of that at 1 C.
Fig. S8  Nyquist plots of the pristine and the Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F at the open circuit voltage. The frequency range is from 100 kHz to 0.1 Hz.

Figure S8 shows the Nyquist plots of the pristine and the Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F at the open circuit voltage. The high-medium frequency semicircle is related to the charge transfer resistance ($R_{ct}$), and the low frequency slope region represents lithium ion diffusion in bulk material. It can be clearly seen that the charge transfer resistance of the 0.5 Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F is much larger than that of the other three samples. The excess amount of Li$_3$PO$_4$ with poor electronic conductivity coating on the surface of active material goes against the charge transfer, and then affects rate performance.
Fig. S9  The first charge/discharge profiles (a) and cycling performances (b) of the pristine Li$_2$CoPO$_4$F in electrolyte with and without LiBOB additive at 5 C and 20 C current rates.

Figure S9 shows the first charge/discharge profiles and cycling performances of the pristine Li$_2$CoPO$_4$F in electrolyte with and without LiBOB additive. Li$_2$CoPO$_4$F in electrolyte with LiBOB additive shows similar charge/discharge profile compared to that in electrolyte without LiBOB additive at 5 C. However, the discharge capacity and working voltage decrease at 20 C for the case in electrolyte with LiBOB additive. It can be seen that LiBOB electrolyte additive can improve the cycling performances at both 5 C and 20 C current rates. These results are similar to that of the Li$_3$PO$_4$-coated Li$_2$CoPO$_4$F in electrolyte with and without LiBOB additive.
Table S1  The initial coulombic efficiencies for the Li$_2$CoPO$_4$F samples at various rates.

<table>
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Table S1 summarizes the initial coulombic efficiencies for the Li$_2$CoPO$_4$F samples at various rates.

It can be seen that the surface modification and electrolyte additive can improve the initial coulombic efficiency compared with the pristine sample at various rates, especially at low current rate. It is believed that surface modification and film-forming electrolyte additive can reduce the contact area between active material and electrolyte, and then reduce the decomposition of electrolyte.